Empirical Force Field Calculations on Tetraarylmethanes and -silanes. I. Static Stereochemistry

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Abstract: The minimum energy conformations on the potential hypersurfaces of a series of tetraarylmethanes and -silanes have been computed by the method of full relaxation empirical force field calculations. In contrast to earlier results from an X-ray diffraction study and crude force field calculations, each of which indicated S_4 symmetry for tetraphenylmethane, the current work gives a ground state of D_{2d} symmetry. On the other hand, tetraphenylsilane is found to have a ground state of S_4 symmetry, consistent with earlier diffraction data and force field calculations, but contrary to the capped C_3 propeller suggested on the basis of Rayleigh scattering experiments. The tetra-*o*-tolyl derivatives of carbon and silicon have calculated ground states of S_4 symmetry, with all substituents oriented exo. Five other diastereomeric conformers based on S_4 symmetry are found for each species, the increase in strain energy correlating approximately with the number of endo substituents. Accordingly, these molecules exist in two meso and four *dl* forms. Results of calculations on other *o*-tolyl and 2,6-xylyl derivatives of tetraphenylmethane lend support to our principal finding that tetraarylmethanes and -silanes (with the single exception of tetraphenylmethane itself) prefer S_4 or ψ-S_4 symmetry, and that, as expected, the environment of exo substituents is less congested than that of endo.

Our interest in the problem of isomerism and isomerization in molecules possessing two or more aryl rings bound to a central atom[1] has recently been extended to the tetraarylmethane series.[2,3] In contrast to the much studied di- and triaryl species,[1] only a first step[3] has been taken in the treatment of the static and dynamic stereochemistry of tetraaryl derivatives. In continuation of our earlier study,[3] we have investigated these systems by full relaxation empirical force field calculations. The present paper details our results on the calculated ground states of these structures (static stereochemistry), while the dynamic aspects of the problem (stereoisomerization) are relegated to a subsequent paper.[4]

As previously discussed,[3] the superimposition of four twofold rotors (in this case, phenyl groups) onto a skeleton of T_d symmetry brings about the removal of all four threefold symmetry axes and the Ar_4Z system can therefore never adopt T_d symmetry, but must belong to one of the seven subgroups of D_{2d}. The D_{2d} subgroup lattice is presented in Figure 1, each of the point groups being exemplified by tetraphenylmethane (TPM) in an appropriate conformation. Two distinct conformations of D_{2d} symmetry exist (**1** and **2** in Figure 1). We find it convenient to refer all other geometries back to these two, which we designate as *closed* ($^cD_{2d}$) and *open* ($^oD_{2d}$) to describe the appearance of the faces of the phenyl rings when the molecule is viewed down the S_4 axis in each of the two D_{2d} conformations (**1** and **2**, respectively).[5]

The relative orientations of the phenyl groups with respect to rotations about the bonds to the central atom, Z, may be defined with reference to the $^cD_{2d}$ conformation (**1**) by a dihedral angle, ϕ, given as the angle between the plane of the phenyl ring and a plane containing both the $C_{central}$–C_{phenyl} bond and the S_4 axis, as shown in Figure 2. In the $^cD_{2d}$ conformation, ϕ is defined as zero for each phenyl ring, and is arbitrarily given a positive value for clockwise rotation of a phenyl group when viewed from the center of the molecule (thus in Figure 2b, ϕ is negative). We shall henceforth give ϕ for each ring in terms of the single acute angle determined according to the above description (Figure 2b). Hence, $\phi = 90°$ for each of the four phenyl rings in the $^oD_{2d}$ conformation (**2**).

If one pair of phenyl rings (i.e., two rings related by the operation of the unique C_2 rotation ($S_4{}^2$)) is open, and the other pair closed, the symmetry is lowered to a unique[5a]

conformation of C_{2v} symmetry, **3** in Figure 1. On the other hand, an infinite number of conformations, differentiated only by the values of the torsional angles, ϕ, exist for all the other allowable point groups. Thus, the S_4 continuum (**4**, Figure 1) is generated by rotating one pair of phenyl groups of either D_{2d} conformation in a clockwise direction ($\phi \neq n\pi/2$ rad, n = integer), and the other pair by an equal amount in the counterclockwise direction. For every full rotation (2π rad) of the phenyl rings, each of the D_{2d} conformations will be traversed twice, and since the S_4 axis retains its position in space, we can unambiguously define ϕ as above.

Rotation of the phenyl rings in either **1** or **2** by equal amounts in the *same* direction leads to an arrangement of D_2 symmetry (**5**, Figure 1). However, rotation by only $\pi/6$ rad suffices to pass from **1** to **2** and vice versa as a result of a simultaneous reorientation of the S_4 axis. Each of the minor C_2 axes in **1** or **2** becomes an S_4 axis in turn as ϕ is incremented by $\pi/6$ rad, so that each of the D_{2d} conformations is passed through six times for every full cycle (2π rad) of the phenyl ring rotations.

Additional distortions of the molecule result in a desymmetrization of the structure, as depicted in Figure 1. Only one example is given for TPM in each of the C_s and C_2 point groups, but others are easily envisaged: for example, a pair of open (rather than closed) phenyl rings could be bisected by the mirror plane in **6**, or a C_2 conformation may be imagined which is based on distortion of a D_2 arrangement, rather than S_4 as shown in **7**. Obviously, any conformation of TPM not falling within one of the aforementioned point groups must be of C_1 symmetry.

Introduction of substituents into ortho or meta positions of the phenyl groups of tetraphenylmethane can lead to a further lowering of the symmetry of the molecule. We shall adopt the convention of modifying the appropriate Schoenflies point group symbol by the prefix ψ when dealing with molecules whose conformations would closely approximate that particular point group in the absence of substituents.

A prime question to be addressed in a study of the static stereochemistry of systems of the type Ar_4Z concerns molecular symmetry, and it was therefore of interest to examine previous literature reports on this subject. X-Ray data on the group 4 derivatives,[6] and some of their perfluorinated analogs,[7] tetraphenylphosphonium[8] and -bismuthonium
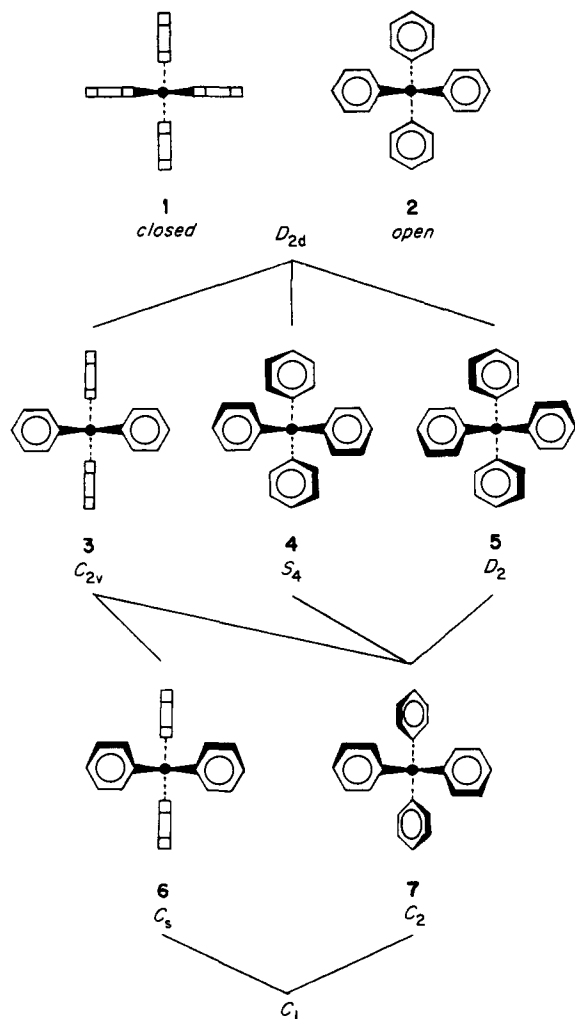
Figure 1. Sketches depicting six of the seven point group symmetries of tetraphenylmethane. The arrangement shown corresponds to the subgroup lattice of the point group D_{2d}.

ions,[9] and in some cases the tetraphenylarsonium ion,[10,11] all indicate that molecular S_4 symmetry is adopted in the crystal. Significantly, in the light of our findings on TPM (see below), tetraphenylborate anion has S_4 symmetry in the presence of unsymmetrical gegenions,[14] but with potassium and tetramethylammonium cations exact $°D_{2d}$ symmetry is found.[15] A gas phase electron diffraction study of tetraphenylsilane also indicates S_4 symmetry;[16] moreover, the results of crude empirical force field calculations[6e,g,14a,17] are consistent with the X-ray diffraction data.

In contrast, it has been reported that molecular optical anisotropy measurements by a depolarized Rayleigh scattering technique for dilute solutions of tetraphenylsilane, -stannane, and -plumbane and tetrakis(p-isopropylphenyl)silane are in accord with a structure best described as a capped propeller (**8**), rather than as one having S_4 symme-

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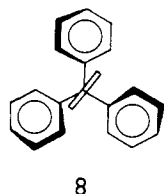
try;[18] it has been claimed[18] that for the S_4 conformation consistency with the experimental results would require an
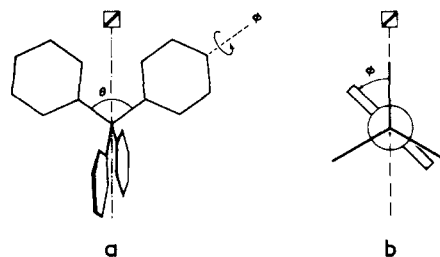
Figure 2. (a) Tetraphenylmethane in the closed D_{2d} conformation. One of the six central valence bond angles, θ, and one of the four torsional angles of twist ϕ are shown. In this case, all four $\phi = 0°$. (b) A Newman projection along a phenyl–C bond, indicating the convention for measuring ϕ (see text).

unacceptably close approach of the ortho hydrogens to each other.

In the only reported isolation of different stereoisomers of an Ar$_4$Z compound, Gilman and coworkers[19] claimed for tetra-o-tolylsilane (TTS) that "it is possible to construct no fewer than eight models of the molecule, representing four meso compounds and two racemic pairs". Subsequently, Cahn, Ingold, and Prelog[20] reasoned that nine isomers (three meso forms and three racemic pairs) are possible for TTS.

In the light of the existing body of knowledge, our inquiry focused on the following questions. (i) Is the preference for S_4 symmetry as general as implied by the structural data on the tetraphenylmethane cognates? (ii) What are the effects of phenyl ring substituents on the preferred geometry and isomer count? (iii) How does the energy of a species vary among its different conformers, and hence what are the relative populations of these conformers?

Method

We have employed the *full relaxation* empirical force field approach to calculate[21] steric energies[22] and geometries of structures corresponding to minima on the potential hypersurfaces for a series of tetraarylmethanes and tetraarylsilanes. Details of the general method have been provided in an earlier paper.[1h] In addition to the empirical force field parameters employed in this earlier study,[23] parameters were introduced for the treatment of interactions involving silicon (Table I), which were taken in part from the work of Tribble and Allinger.[24]

The "pattern search" method was again used throughout our study to effect computational strain energy minimization.[25] Our general approach has been to minimize fully the strain energy of a required starting structure allowing full relaxation of all atoms. The resultant minimization normally involved particular ring torsions, and to ensure that we had reached a true minimum, an attempt was made to arrive at the same final structure from a starting conformation whose minimization involved rotation of the aryl rings in the *opposite* direction. Thus, we shall henceforth speak of minima which have been approached "from both sides". In other cases, an initial structure might have partially minimized into a channel whose ultimate fate was known precisely from previous calculations. Such calculations were terminated at that stage.

In using the technique of approaching the minimum from both sides, a few molecules were found to give apparently different minima, usually because the true minimum was situated in or near an extensive flat region of the potential hypersurface. This difficulty was overcome by calculating the geometries and energies of a few intermediate points on the surface by artificially incrementing one or more molec-

Table I. Empirical Force Field Parameters for Tetraarylsilanes[a,b]

	Stretch[c]	
	k_r	r^0
$C_{ar}-Si$	2.97	1.850

	Bend	
	k_θ	θ^0
$C_{ar}-Si-C_{ar}$	0.48	109.5
$C_{ar}-C_{ar}-Si$	0.35	120.0

	Twist			
	V_0	B	n	ϕ_{max}
$C_{ar}-C_{ar}-Si-C_{ar}$	0.014	1.0	6	30
$H-C_{ar}-C_{ar}-Si$	0.0			
$C_{sp^3}-C_{ar}-C_{ar}-Si$	0.0			
$C_{ar}-C_{ar}-C_{ar}-Si$	0.0			

	Nonbonded[c]	
x	$\frac{1}{2}d_{xx}*$	ϵ_{xx}
Si	1.780	0.044

	Out-of-Plane	
	k_δ	δ^0
$(C_{ar}-C_{ar}-C_{ar})-Si$	0.80	0.0

[a] Potential functions are given in eq 1 of ref 1h. Table 1 (ref 1h) should be consulted for those empirical force field parameters which involve only carbon and hydrogen. [b] The following units apply: ångstroms (r^0 and $d*$); degrees (θ^0, δ^0, ϕ_{max}); millidynes ångstroms^{-1} (k_r); millidynes radians^{-2} (k_θ, k_δ); kcal/mol (V_0, ϵ). [c] Taken from ref 24.

Figure 3. Strain energy of tetraphenylmethane (TPM) in the S_4 (D_{2d}) conformation as a function of the torsional angles of the phenyl rings. Curve a: nonrelaxed force field, using the nonbonded parameters of Kitaigorodsky and coworkers (ref 17). Curve b: nonrelaxed force field using the nonbonded parameters of the present work (ref 1h). Curve c: full relaxation force field. Note that curve "b" is offset by about 22 kcal/mol with respect to "a" and "c".
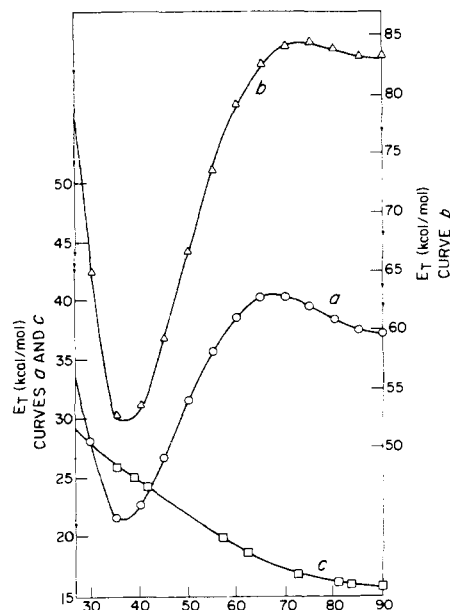
ular parameters—usually the dihedral angles, ϕ, of each apparent minimum—by a small amount, and allowing further minimization with full relaxation. In this way, we were able to determine the geometric features of the surface, and magnitude of the potential energy barrier, if any, between the two apparent minima. This method of surface exploration will henceforth be referred to as method I.

In other circumstances, largely confined to our studies of conformational dynamics,[4] we were interested in determining the strain energies of structures which did not correspond to minima on the potential hypersurface. To prevent retrograde minimization to the starting structure, itself a minimum, it was necessary to lock the coordinates of some atoms. Hence, although total relaxation of all other atoms was permitted, the new structure obviously could not correspond to a fully minimized point on the surface, although it might be a good approximation thereof. Calculations effected in this manner will be described as method II minimizations.

Our confidence in the remarkably high accuracy of this general technique for predicting both energetic and structural parameters of polyaryl derivatives is based on the results of earlier, closely related work.[1h] Not only does the program accurately predict the activation energy for the threshold stereoisomerization of trimesitylmethane (calculated 20 kcal/mol; experimentally found 21.9 kcal/mol), but the recently determined crystal structure of this compound[26] agrees nicely with the calculated ground state.

Results and Discussion

Tetraphenylmethane and Tetraphenylsilane. The energy of TPM in the S_4 (D_{2d}) conformation has been calculated by Kitaigorodsky and coworkers[17] as a function of ϕ on the assumption of *fixed* values for all other molecular parameters. Only intramolecular nonbonded interactions were considered in computing the energy of the molecule. A ground state of S_4 symmetry ($|\phi| = 37°$) was found, as well as a high energy minimum corresponding to the $°D_{2d}$ conforma-

tion. Using the reported[17] nonbonded parameters, we obtained essentially the same potential energy curve as reported (curve a, Figure 3); using our normal nonbonded function[1h] we obtained the potential surface depicted by curve b in Figure 3, which exhibits the same trends but which has a relatively deeper minimum corresponding to the S_4 ground state. After making due allowance for *inter*molecular nonbonded forces, Kitaigorodsky and coworkers were able to show that their crude force field calculations were sufficiently refined to reflect the molecular geometry of TPM in the crystalline state.

In startling contrast to the situation described above, calculations starting from a variety of conformations, and using *full relaxation* minimization techniques, revealed only a single minimum on the potential hypersurface of TPM, that corresponding to the $°D_{2d}$ conformation (Table II). Calculation of the total steric energy corresponding to a number of structures along the S_4 channel by method II gave the potential energy curve c depicted in Figure 3. It is clear that there is not even an inflection in the region where the crude calculations had predicted minima of S_4 symmetry. The contrast with the earlier calculations[17] is even more striking when it is recalled that our nonbonded parameters emphasize the tendency of the nonrelaxed molecule to adopt an S_4 ground state (curve b, Figure 3).

Repetition of the full relaxation calculations using our alternative nonbonded function parameter sets A, B, and D[1h] caused no significant change in the final minimum energy conformation, and increase of the angle bending parameter for the central bond angles, k_θ, by a factor of 2.5 likewise had no effect.

The situation becomes even more intriguing when we consider the corresponding silane, TPS. Kitaigorodsky and coworkers[17] had earlier shown, by use of their crude calculations, that the surface for TPS exhibits essentially the same features as in TPM, but with a much lower barrier for the interconversion of the S_4 global minimum[16] to the $°D_{2d}$ local minimum. In this case, our full relaxation calculations

Table 11. Conformers of Tetraarylmethanes and -silanes, Their Absolute Strain Energies and Molecular Parameters, and Input Data for Strain Minimizations

Input structures[a]	Minimized structure[b] Designation[a]	Symmetry	$E_T{}^c$	r^d	ϕ^d	θ^e	
			Tetraphenylmethane (TPM)				
1, 2, 4, 8	2	$^oD_{2d}$	15.9	1.555	+88.8	96.9	116.1
				1.554	+88.5	97.0	116.0
				1.554	−88.8		116.1
				1.553	−89.2		116.0
			Tetraphenylsilane (TPS)				
4, 8	4*	S_4	−2.9	1.869	−39.8	109.7	109.3
				1.869	−39.8	109.6	109.4
				1.869	+39.8		109.4
				1.869	+39.8		109.4
1, 2	2	$^oD_{2d}$	−2.6	1.865	90.0	103.4	112.5
				1.865	90.0	103.3	112.7
				1.865	90.0		112.5
				1.865	90.0		112.7
			Tetra-o-tolylmethane (TTM)				
16, (xxxx)	(xxxx)	S_4	35.5	1.570	−54.9	100.6	114.2
				1.569	−55.3	100.8	113.9
				1.569	+55.0		113.9
				1.570	+54.9		114.1
11, 12, 13, 14, (xxnn)	(xxnn)*	C_2 (ψ-S_4)	38.8	1.567	+62.3	97.8	118.1
				1.567	+62.4	98.2	113.0
				1.572	−67.9		113.1
				1.571	−68.1		117.9
15, 10, 17, 18, (xxxn)	(xxxn)	C_1 (ψ-S_4)	39.6	1.561	+54.8	99.7	116.9
				1.572	+56.3	101.2	113.3
				1.576	−59.4		111.1
				1.570	−57.1		115.2
(nnxn)†	(nnxn)	C_1 (ψ-S_4)	42.4	1.566	+61.1	98.4	115.1
				1.575	+64.6	99.1	118.1
				1.573	−59.1		114.5
				1.568	−58.0		112.5
19, 20, 21	(nxnx)	C_1 (ψ-S_4)	43.8	1.563	−61.7	98.6	114.6
				1.578	−66.2	98.9	118.3
				1.574	+61.3		113.1
				1.569	+64.4		114.2
(nnnn)	(nnnn)	S_4	58.1	1.584	−7.7	126.8	101.6
				1.584	−7.7	126.4	101.4
				1.583	+9.7		101.7
				1.583	+8.4		101.9
			Tetra-o-tolylsilane (TTS)				
16, (xxxx)	(xxxx)	S_4	2.2	1.880	+50.4	104.5	112.0
				1.880	+50.6	104.6	112.0
				1.880	−50.6		112.0
				1.880	−50.4		111.9
(xxnx)†	(xxnx)	C_1 (ψ-S_4)	5.7	1.875	−48.9	104.6	113.1
				1.885	−48.5	104.7	112.9
				1.887	+54.0		112.8
				1.885	+50.7		109.0
12, (nnxx)	(nnxx)*	C_2 (ψ-S_4)	6.9	1.884	−70.3	100.9	114.9
				1.882	−70.5	101.2	112.9
				1.881	+58.9		112.7
				1.880	+59.1		114.9
17, (nxxn)	(nxxn)	C_1 (ψ-S_4)	9.1	1.879	+51.4	102.9	116.3
				1.887	+51.6	104.6	113.0
				1.883	−49.5		109.7
				1.888	−52.6		110.4
12	13	D_2	10.5	1.888	+87.4	101.4	109.9
				1.889	+87.4	101.5	117.4
				1.889	+87.3		117.4
				1.889	+87.3		109.9
(xxnx), (xnnn)	(xnnn)*	C_1 (ψ-S_4)	10.6	1.884	−66.6	100.2	116.6
				1.881	−62.2	99.5	111.9
				1.876	+71.3		115.5
				1.885	+70.5		113.9
(nnnn)†	(nnnn)	S_4	17.4	1.903	+16.4	114.6	107.1
				1.902	+16.6	114.5	107.0
				1.902	−16.4		106.9
				1.902	−16.6		107.0
			Triphenyl-o-tolylmethane				
22, 23, 24, (n000)†	(x000)	C_1 (ψ-S_4)	21.8	1.563	−71.1	99.3	115.1
				1.557	−65.6	96.9	116.3
				1.557	+72.0		117.2
				1.558	+70.8		113.1

Table 11. *(Continued)*

Input structures[a]	Minimized structure[b]		$E_T{}^c$	r^d	ϕ^d	θ^e	
	Designation[a]	Symmetry					
Triphenyl(o-tert-butylphenyl)methane							
25	(x000)	C_1	41.1	1.573	+73.4	102.8	118.4
	(ψ-S_4)			1.561	+47.4	97.6	111.4
				1.570	−61.9		107.0
				1.561	−67.7		120.6
Diphenyldi-o-tolylmethane							
26, (x0x0), (x0n0)	(x0x0)	C_1	26.8	1.564	−64.3	99.7	115.6
	(ψ-S_4)			1.561	−56.2	99.8	115.3
				1.559	+58.5		114.3
				1.566	+62.7		113.0
27, (xx00)	(xx00)	C_2	27.1	1.564	+56.1	102.5	116.3
	(ψ-S_4)			1.564	+56.0	98.6	111.8
				1.563	−59.6		111.9
				1.563	−59.7		116.5
28, (n0n0)†	29	C_1	27.1	1.564	+72.1	97.8	116.6
	(ψ-S_4)			1.562	+70.8	97.2	117.3
				1.562	−69.5		117.2
				1.561	−66.3		111.9
30, (nn00)	31*	C_1	27.2	1.566	−76.0	96.8	117.9
	(ψ-S_4)			1.555	−69.5	96.7	113.6
				1.565	+75.0		113.2
				1.560	+76.4		120.1
(xn00)†	(xn00)	C_1	31.0	1.570	−62.6	101.4	114.2
	(ψ-S_4)			1.565	−58.0	97.4	114.5
				1.558	+59.8		118.1
				1.565	+62.7		112.1
Triphenyl-2,6-xylylmethane							
32, 33	*	C_1	29.7	1.567	−73.4	100.3	114.3
	(ψ-S_4)			1.561	−61.5	95.2	117.6
				1.562	+71.4		117.9
				1.556	+68.8		112.6
Diphenylbis(2,6-xylyl)methane							
34, 35		C_1	43.3	1.575	−77.1	96.4	117.4
	(ψ-S_4)			1.564	−63.8	96.3	117.0
				1.568	+67.8		115.2
				1.571	+74.4		116.4
36, 37		C_2	51.2	1.579	−66.0	106.9	115.0
	(ψ-S_4)			1.578	−66.2	91.5	114.3
				1.564	+65.4		114.0
				1.564	+66.0		114.9
Tetrakis(2,6-xylyl)methane							
38, 39†, 40		S_4	84.3	1.586	+52.9	99.4	114.3
				1.587	+53.0	99.2	115.3
				1.585	−53.6		115.3
				1.585	−53.5		114.2

[a] Numbers refer to structures given in Figures 1 and 7 and in the text. The designations refer to S_4 or ψ-S_4 structures, as defined in the text. The descriptors x and n apply to aryl groups 1 through 4 sequentially, with reference to the reference structure 1 (see below). Structures differing in torsional angles, ϕ, but otherwise identical, were used as input in some instances (marked with a dagger (†)).


reference structure I
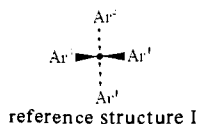
[b] Conformers marked with an asterisk (*) were found by method 1 minimization (see text). All others were derived by minimizations from both sides, or, in three cases, by a single minimization. [c] E_T's (kcal/mol) are to be compared directly only for isomeric structures; see text. [d] Recorded sequentially for aryl groups 1 through 4 with reference to reference structure I, which is viewed down the S_4 or ψ-S_4 axis. See Figure 2 for the convention for measuring ϕ. [e] Recorded as the valence angles defined at the central atom (reference structure 1) by aryl groups 1 and 2, and 3 and 4 (left column), and groups 1 and 3, 1 and 4, 2 and 3, and 2 and 4 (right column), respectively. This division, which corresponds to the two sets of symmetry equivalent angles in an S_4 structure, is not applicable to the conformer of D_2 symmetry (13), whose central valence angles are necessarily divided into three sets of two. For convenience, however, the same arrangement is adopted in the table.

give almost the same conclusion; in contrast to TPM, the silane has a ground state of S_4 symmetry, and a secondary shallow minimum with the $^oD_{2d}$ conformation (Table II and curve a, Figure 4). However, the barrier determined by use of method I for the $S_4 \rightarrow {}^oD_{2d}$ isomerization is less than 0.3 kcal/mol, whereas the nonrelaxed calculations give a value of 3 kcal/mol.[17]

An analysis of the structure–strain relationships for the two tetraphenyl derivatives reveals features which suggest a likely reason for the observed difference in energy and stereochemistry.

The chief source of strain in the nonrelaxed molecules of $^oD_{2d}$ symmetry involves nonbonded repulsions between those pairs of phenyl rings which are related by the S_4 oper-
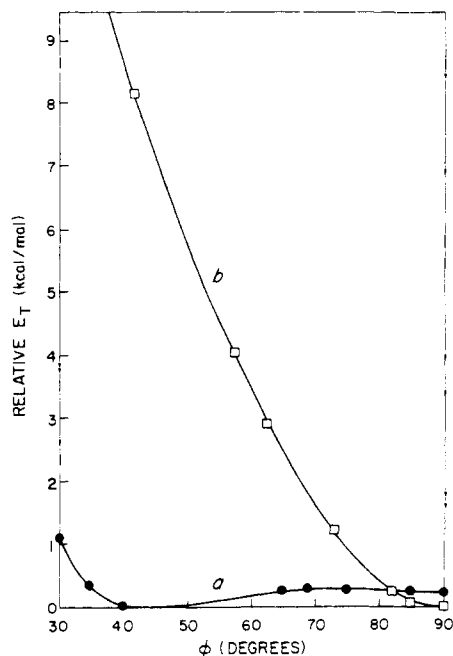
Figure 4. Strain energy of tetraphenylsilane (curve a) and tetraphenylmethane (curve b) in the S_4 (D_{2d}) conformation as a function of ϕ. Although absolute strain energies cannot be compared, it is valid to compare *differences* in E_T for the two species over identical ranges of ϕ.

ation as indicated by the arrows in the $^\circ D_{2d}$ conformation shown below (**9**). This strain may be relieved by several re-

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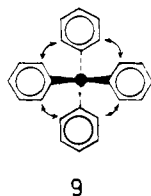
laxation modes. First, some bonds, particularly the four to the central atom, may stretch. Second, valence angles may change; in particular the two angles bisected by the S_4 axis will tend to contract, and the other four correspondingly enlarge. Third, the aryl rings may depart from their idealized regular planar hexagonal symmetry, as is in fact observed in all the systems we have studied. Finally, rotation of the rings about the central bonds can lead to an overall decrease in nonbonded repulsions through more favorable separations of interacting centers.

The crude calculations allow for only one relaxation mode, i.e., phenyl ring torsions, and each of the three main contributing nonbonded interaction types ($H \cdots H$, $H \cdots C_{aromatic}$, and $C_{aromatic} \cdots C_{aromatic}$) possess their deepest minima at essentially the same value of ϕ (i.e., at ca. 35°). This effectively accounts for the preference for an S_4 ground state by both TPM and TPS, as determined by these crude calculations. However, full relaxation calculations additionally permit all other relaxation modes. The result of angle bending is to increase the separation of the sterically offending groups at the cost of a relatively small increase in angle bending strain. Both TPM and TPS adopt this latter relaxation mode (see Table II) to give their respective minima of $^\circ D_{2d}$ symmetry, and the methane also exhibits lengthening of the four bonds to the central carbon from a preferred value of 1.50–1.51 to 1.55 Å.[27]

For the methane, any distortion of this arrangement which results from rotation of the rings into an S_4 confor-

mation introduces only unfavorable interactions between the previously noninteracting pairs of phenyl rings, and the result in this case is that all S_4 conformations are higher in energy than the unique $^\circ D_{2d}$ ground state. Summarizing, in the methane, relief of strain by central bond angle distortions far outweighs any relatively minor energy gain resulting from rotation of the rings into an S_4 conformation.

By comparison with the methane, the silane is inherently less hindered by virtue of its longer central bonds,[6b,c] so that if rotation in an S_4 channel is coupled with relaxation of the central angles back to the preferred value (in our case 109.5°, as in Table I), the strain of the molecule is ultimately slightly decreased to the S_4 ground state as depicted in Figure 4.

We had noted earlier a report[18] that TPS and related molecules cannot adopt S_4 symmetry and that a "capped propeller", **8**, is more consistent with the data. However, two features emerge from our calculations which lead us to reject the proposed structure (**8**). First, when used as input, **8** minimizes into the S_4 manifold, a result which is in direct contrast to the order of stabilities proposed by the French workers.[18] Second, we find that in TPS of S_4 symmetry ($|\phi| = 69°$),[28] containing idealized bond lengths and angles, the shortest $H \cdots H$ intramolecular separations are wholly compatible with normally accepted values,[29] contrary to the criterion which had led the earlier workers[18] to reject the S_4 conformations.

Of particular interest is a comparison between the calculated structures of TPM and TPS and the structures found in the crystal. The silane in the solid is reported[6c] to be of S_4 symmetry, with $|\phi| = 44°$. Our calculated value of 40° for the S_4 structure is in accord with this report. Furthermore, our force field yields a value for the carbon–silicon bond length of 1.869 Å, comparing favorably with 1.876 Å[6b] and 1.872 Å[6c] in the crystal, and values of bond angles at silicon of 109.6° and 109.4° for the two types of symmetry-differentiated angles, which are to be compared with the experimentally determined values of 107.7°[6b] (107.4°[6c]) and 110.3°[6b] (110.5°[6c]), respectively. In contrast, the energy of the calculated ground state of TPM is approximately 5 kcal/mol *below* a structure of S_4 symmetry with the same value for the phenyl twist angle as that reported for the molecule in the crystal ($|\phi| = 55°$);[6a] see Figures 3 and 4. A reasonable explanation for this apparent contradiction is that *inter*molecular forces are sufficiently strong to overcome the energy needed to effect the conformational change from $^\circ D_{2d}$ symmetry in the free state to S_4 symmetry in the crystal.[30] Evidence bearing on this postulate derives from structural data on the tetraphenylborate anion,[14,15] a species whose central bond length (1.64 Å) is intermediate between those of TPM and TPS, and which might therefore reflect properties associated with each of these. As we noted in the introductory section, the symmetry assumed by the anion (S_4 vs. $^\circ D_{2d}$) is a function of the associated cation; obviously intermolecular forces in the crystal are dictated by packing density, and as a result of the separation of the anions and the symmetrical nature and positioning of the cation in the lattice, intramolecular forces play the dominant role in determining the anion stereochemistry in the K^+ and the $(CH_3)_4N^+$ salts.[15] The analogy between TPM and the boron analog is reinforced by the similarity of the distortions which the two systems suffer at the central atom. Thus, two angles in the anion are compressed to 102.7° (K^+) or 102.1° ($(CH_3)_4N^+$), while the other four are enlarged to 112.9° (K^+) or 112.3° ($(CH_3)_4N^+$),[15] precisely as in TPM (see Table II).

Tetra-*o*-tolylmethane and -silane. Interest in these compounds derives from the work of Gilman and coworkers,[19]
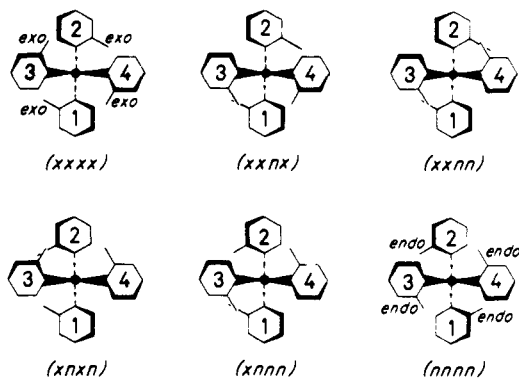
Figure 5. The six diastereomeric conformations of tetra-*o*-tolylsilane having S_4 or ψ-S_4 symmetry. For notation, see text.

METHYL STEREOCHEMISTRY

Figure 6. Strain energies of the conformers of tetra-*o*-tolylmethane (□) and -silane (●) as a function of exo (*x*) and endo (*n*) orientation of the methyl substituents. For notation, see text.

who addressed the question of stereoisomerism in tetra-*o*-tolylsilane (TTS). For this molecule, as well as for the related tetra-*o*-tolylmethane (TTM), six and only six diastereomeric conformers with S_4 or ψ-S_4 symmetry are possible and are depicted in Figure 5. For the purpose of the present discussion, we introduce an isomer designation scheme based on the endo–exo description introduced in our earlier paper.[3] This nomenclature serves to distinguish the different edges of the phenyl groups, those inclined toward the center of the molecule being labeled endo, and those inclined away from the center exo. If we let the descriptors *n* and *x* refer to the edges, endo and exo, respectively, which bear the methyl substituents, a sequence of four descriptors will then suffice to define the diastereomer unambiguously, with the additional convention that the first two descriptors of each sequence correspond to a pair of *o*-tolyl groups related by a $C_2(S_4^2)$ or ψ-$C_2(\psi$-$S_4^2)$ rotation and the second two to the other pair. As seen in Figure 5, the (*xxxx*) and (*nnnn*) forms have S_4 symmetry, the (*xxnn*) form has C_2 symmetry, and the other four diastereomers are asymmetric, though of ψ-S_4 symmetry.

To determine the structure and energy of the various possible conformers of TTM, a diverse selection of input structures (Table II) was subjected to energy minimization. Only six diastereomeric structures were found which corresponded to minima on the potential hypersurface; these are the six diastereomers of S_4 or ψ-S_4 symmetry described above (Figure 5). Calculations on the analogous silane, TTS, gave parallel results. Six diastereomers of S_4 or ψ-S_4 symmetry were found, with one possible additional conformer of D_2 symmetry which will be discussed below.

Of the six S_4 or ψ-S_4 conformers obtained for each of these series, four are chiral, resulting in a total of ten isomers for TTM and for TTS (two meso forms and four *dl* pairs). As was noted in the introductory section, Gilman and coworkers had earlier postulated four meso forms and two *dl* pairs for TTS on the basis of an examination of molecular models.[19] In view of the present results, this conclusion must now be revised. Consideration of subsequent suggestions by Cahn, Ingold, and Prelog[20] is more suitably delayed for discussion in the subsequent paper.[4]

The relative strain energies of the conformers of TTM and TTS are displayed in Figure 6. In each case, the ground state is the (*xxxx*) isomer (S_4 symmetry). In both the methane and silane series, this conformer is sufficiently lower in energy than the conformer of next highest energy to render the (*xxxx*) isomer the only significantly populated species at normal temperatures. We have already made use of this fact in our interpretation of the dynamic behavior of TTS and related molecules.[2,3]
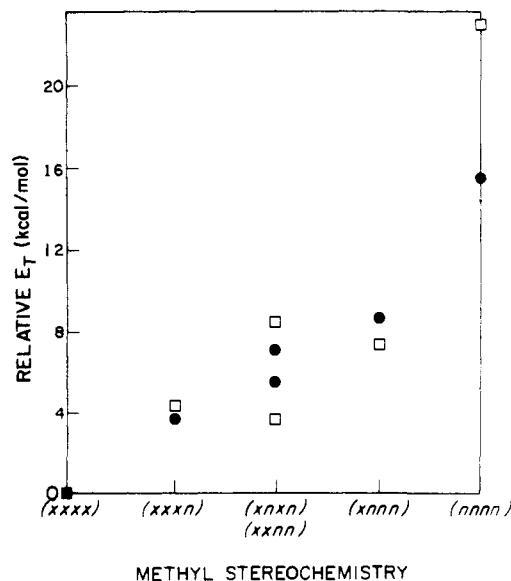
With reference to Figure 6, similar though not identical trends in energy are noted for the two species as the *o*-methyl groups become successively oriented endo. The trends are in the expected direction since switching a methyl substituent from the relatively unencumbered exo side to the sterically congested endo position will be accompanied by unfavorable nonbonded interactions. We believe that a more detailed analysis, particularly with regard to the irregularities in the trends, is unwarranted at this time.

It is of interest to consider the relaxation modes these molecules employ to reduce their inherent strain. The central bond length increases in TTM are unusually large (Table II).[27] In all conformers of TTM and TTS the methyl groups are bent away from the central atom by at least 4° from the "ideal" value of 120° but out-of-plane deformations are disfavored. The methyl group is further effectively removed from the center of crowding by an increase in the valence angle subtended at the aromatic ring carbon which is bonded to the central atom and the methyl-substituted *o*-carbon atom. As in tetraphenylmethane, deformation of the central bond angles in TTM and TTS follows a characteristic pattern for most conformers. Interactions between adjacent rings are most easily relaxed by a motion of the C_2-related rings toward each other, and a concomitant closing up of the two respective central angles which are bisected by the S_4 or ψ-S_4 axis. This relaxation mode is apparent for all conformers except the highest in energy for both the methane and silane. The isomer of highest energy, (*nnnn*) in each case, adopts the exact reverse central angle relaxation mode. In order to overcome the four severe endo-methyl interactions with adjacent rings, these *o*-tolyl groups rotate so that the methyls are beyond the position for worst interactions with their adjacent groups (i.e., to low $|\phi|$ values). However, as a consequence, the repulsive H····H interaction between opposite *o*-hydrogen atoms becomes intense, and to ameliorate this situation, pairs of opposite aryl groups separate by *opening* the two central angles to the extraordinary value of 126.6° for (*nnnn*)-TTM and to 114.5° for (*nnnn*)-TTS.

We have so far only been concerned with S_4 and ψ-S_4 conformations, which together predominate both for TTM and TTS. However, TTS differs uniquely from TTM in
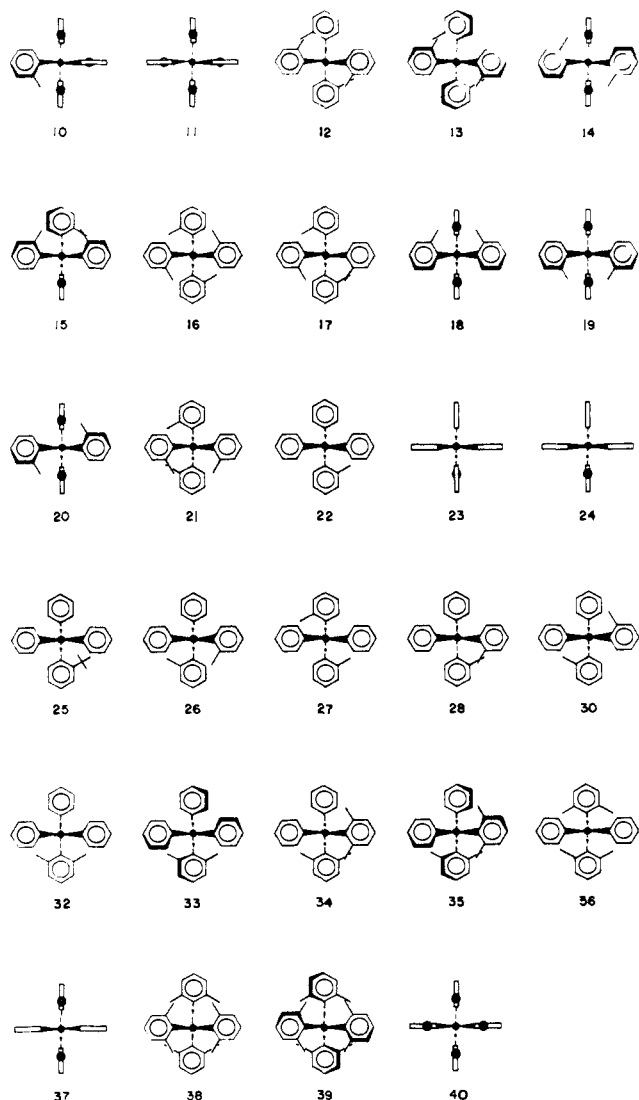
Figure 7. Input structures for strain energy minimization calculations.

If, by analogy with TTM, triphenyl-*o*-tolylmethane prefers to adopt conformations of ψ-S_4 symmetry, only two diastereomeric conformers should exist, one with the methyl group exo (*x*000) and one with the methyl group endo (*n*000).[34] In fact, all input structures (Table II) were found to minimize only to the exo form, even though three of these (two different conformations with stereochemistry (*n*000) and **24**) were specifically designed to find the minimum for the endo form if such existed. In every case a suitable combination of aryl group torsions took the methyl group into the less sterically crowded exo orientation. Substitution of the bulky *tert*-butyl group for the methyl substituent leaves the stereochemistry essentially unchanged (Table II).

In diphenyldi-*o*-tolylmethane, each of the input structures (Table II) led to one of a total of five minimum energy conformations (Table II). If we consider all possible combinations of two *o*-methyl substituents on a tetraphenylmethane skeleton in the S_4 conformation, one to a ring, a total of seven chiral diastereomeric conformations results. The five calculated minima are all members of this set; the two missing isomers are all-endo, (*nn*00) and (*n*0*n*0). That exo substituents are less sterically encumbered than endo is further confirmed by the observation that the two lowest energy conformers are all-exo, (*x*0*x*0) and (*xx*00). However, since the energy of two (*x*0*n*0) conformers, **29** and **31**,

29   31
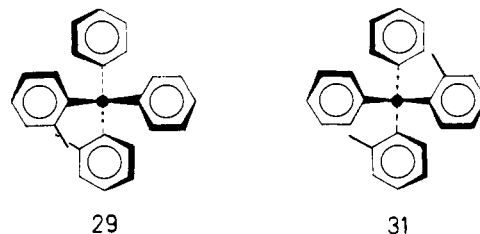
is of the same order, even though each contains one endo substituent, diphenyldi-*o*-tolylmethane has no unique ground state, each of the four conformers (two all-exo and two (*x*0*n*0)) being significantly populated at room temperature. In the fifth conformer, (*xn*00), which also has an endo, exo structure, the substituents are situated on opposite rings of the tetraphenylmethane skeleton, and thus juxtapositioned; the methyl groups interact unfavorably and lead to the observed increase in steric strain.

Both possible all-endo conformations, (*n*0*n*0) and (*nn*00), are notable only for their instability with respect to other conformers. In three attempts to "trap" these as stable conformations, minimization appeared to be finalizing at total steric energies of about 40 kcal/mol, corresponding to structures of the expected geometry. However, prolonged minimization ultimately permitted relaxation by combinations of suitable group rotations into channels leading to **29** and **31**. Thus, the all-endo conformations exist as points of inflection on the hypersurface, or at best as high-energy minima.

The 2,6-Xylylmethane Series. Computations were also performed on a series of molecules containing methyl groups in *both* ortho positions of the phenyl rings of the skeleton.

Only one diastereomeric modification of triphenyl-2,6-xylylmethane is possible if ψ-S_4 symmetry is maintained. Our calculations led to precisely this equilibrium structure. As might be expected, the strain energy of this conformer is of the order of that found for the three *endo,exo*-diphenyldi-*o*-tolylmethane conformers (**29**, **31**, and (*xn*00)).

The next member of this series, diphenylbis(2,6-xylyl)-methane, has the potential to exist in two diastereomeric forms if ψ-S_4 symmetry is preferred. Again, this is precise-

that it also exhibits a species of D_2 symmetry, which may also be a minimum on the potential hypersurface (Table II). The strain energy of this conformer (**13**, Figure 7) is just 0.7 kcal/mol below a structure of ψ-$^oD_{2d}$ symmetry (**12**, Figure 7), a structure which also lies in the S_4 channel and which we have shown to minimize to the (*xxnn*) ψ-S_4 conformer with C_2 symmetry (Table II). While this suggests that the D_2 form is a minimum on the surface, there may be a continuous downhill path from it to the C_2 form passing through C_1 structures, and bypassing the ψ-$^oD_{2d}$ structure. This slight deviation from the otherwise consistent preference for S_4 or ψ-S_4 symmetry may result from the unique combination of nonbonded interactions present in this particular structure. Rather than cause descent into the S_4 manifold, the two pairs of adjacent *o*-methyl groups mutually repel with the result that a D_2 conformation is adopted. At the same time, however, torsion away from the ψ-$^oD_{2d}$ structure is restricted to less than 3°, since the two pairs of *o*-hydrogens are simultaneously forced into unfavorably close positions.

It is these *o*-hydrogen interactions which render the D_2 conformations energetically unfavorable for all other substituent arrangements. In the case of TTM, the inherently shorter *o*-hydrogen separations preclude stability for all D_2 structures.

Triphenyl-*o*-tolylmethane and Diphenyldi-*o*-tolylmethane.

ly what is observed, the asymmetric conformer being more stable by about 8 kcal/mol than the conformer of C_2 symmetry. Such a finding is expected as soon as we recognize the presence of two methyl–methyl interactions between pairs of substituents on opposite aryl groups in the less stable conformer, in contrast to the single neighboring interaction in the more stable form.

The most highly substituted member of this series, tetrakis(2,6-xylyl)methane, is a molecule closely related to tetraphenylmethane in that all four rings are identical and possess local C_2 axes. In contrast to tetraphenylmethane, however, the ground state point group symmetry of the molecule is found to be S_4, and there is no indication of any minimum corresponding to the $^{\circ}D_{2d}$ conformation. The four opposite pairs of methyl groups (situated on rings permuted by an $S_4{}^2$ operation) are highly disfavored in this latter conformation, but the strain is readily alleviated by torsions of the groups to yield a conformation of S_4 symmetry.

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(22) For a definition of the total steric energy, E_T, see eq 1 in ref 1h. A comparison of E_T's for different calculations is valid only when the structures involved are either isomeric or possess the same number and kinds of interactions. In the present paper, we shall be concerned only with the relative conformational energies of a series of conformational diastereomers of a given species, and not with relative energies of constitutionally different molecules.
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(28) Unanue and Bothorel[18] give S_4 structures with $|\phi| = 21°$ or $|\phi| = 69°$ as results derived from their data.
(29) For nonrelaxed TPS, with $|\phi| = 69°$, the shortest H····H separations are between pairs of aromatic hydrogens on the same aromatic ring (2.387 Å). The next nearest approach is 2.484 Å, between ortho hydrogens on adjacent phenyl rings (i.e., those related by an S_4 operation). Unanue and Bothorel give 1.84 Å ($|\phi| = 21°$) and 1.53 Å ($|\phi| = 69°$) for the shortest inter-ring H···H distances.[18]
(30) The crystal packing forces of biphenyl are sufficient to overcome the ca. 1 kcal/mol[31] required to change the preferred D_2 conformation of the unconstrained molecule[32] to the planar structure (close to D_{2h}) found in the crystal.[33] In the present case, we regard the calculated difference in energy between the S_4 and $^{\circ}D_{2d}$ forms of TPM (ca. 5 kcal/mol) as an upper limit, and accept the possibility, inherent in the limitations of the computational method used, that the difference may be a few kilocalories/mole lower.
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